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NEW SYNTHESIS OF VINYL SELENIDES

NUCLEOPHILIC SUBSTITUTIONS OF UNACTIVATED VINYL HALIDES BY SELENIDE ANIONS

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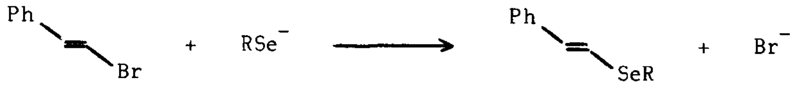
Abstract. Alkyl and aryl selenide anions react with unactivated vinyl halides, in dipolar aprotic solvents, to give alkyl or aryl vinyl selenides in good yields. These reactions are stereospecific and occur with retention of configuration.

Vinyl selenides have attracted considerable attention in the last few years[1-3] in view of their importance as synthetic precursors of several organic compounds.[1] In connection with our recent works on the reactivity of unactivated aryl halides with sodium alkanethiolates[4] or lithium alkyl selenides[5] and of vinyl halides with sodium alkanethiolates,[6] we report a convenient new synthesis of vinyl selenides. Good yields of vinyl selenides are obtained from the reaction of vinyl halides with selenide anions in dipolar aprotic solvents (HMPA, DMF, DMA). These new reactions also have a considerable mechanistic interest since they represent examples of nucleophilic vinyl substitutions occurring on unactivated substrates. As shown below in the case of the (E)- and (Z)-ß-bromostyrenes these reactions are stereospecific and occur with retention of configuration.



The vinylic substrates employed in the present work were the (E)- and (Z)-ß-bromostyrenes, the (E)- and (Z)-1-chloro-2-phenylthioethenes and the (E)- and (Z)-1-chloro-2-phenylselenylethenes.[7] These were allowed to react with MeSeLi (obtained from methyllithium and elemental selenium[5]) and with PhSeNa (prepared from diphenyl diselenide by reduction with sodium in HMPA or with NaH in DMF). Also investigated were the reactions of the two ß-bromostyrenes with the α-$C_{10}H_7SeNa$ and the p-$(Me_2CHS)C_6H_4SeNa$. These aryl selenide anions were obtained from the corresponding methyl selenides by dealkylation with sodium in HMPA or in DMA.[4,5]

A typical experimental procedure is as follows. To a solution of the selenide anion (0.015 mol), in HMPA, DMF or DMA (20 ml), the vinyl halide (0.01 mol) was added and the mixture was stirred under nitrogen at the temperature and for the time indicated in the Table. The progress of the reaction was monitored by glc and tlc. The reaction mixtures were worked up in the usual way and the products were purified by column chromatography.[8] Reaction conditions and reaction yields are collected in the Table. Although HMPA seems to be the most efficient solvent, the results obtained demonstrate that these reactions occur in good yields in DMF or DMA also.

On the basis of the observed stereochemical course we suggest that the reactions described above can be considered as bimolecular substitutions which involve nucleophilic attack at the vinylic carbon atom holding the leaving halogen atom, as suggested in the case of the related reactions effected by the alkanethiolate anions.[6]

Owing to the extremely simple experimental conditions employed and to the good yields obtained the present procedure can be considered a very convenient general method for the synthesis of vinyl selenides.[9]

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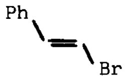
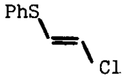
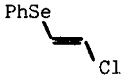
Table^{a}

Vinyl Halide	Selenide Anion	Reaction Temp. (°C)	Reaction Time (h)	Vinyl Selenide^{b}	Yield^{c} (%)	^{1}H-nmr^{d} A	B	J_{AB}
	MeSe	25	0.5 (8)	(E)-PhCH=CHSeMe	82 (79)	7.0	6.55	16.0
	PhSe	120	1 (6)	(E)-PhCH=CHSePh	82 (73)	7.15	6.8	16.0
	α-$C_{10}H_7Se$	120	2.5	(E)-PhCH=CHSe$C_{10}H_7$-α	75	7.05	6.65	16.0
	p-(Me_2CHS)C_6H_4Se	120	5 (12)^{e}	(E)-PhCH=CHSeC_6H_4($SCHMe_2$)-p^{f}	85 (85)^{e}	7.1	6.85	16.2
	MeSe	25	0.5 (4)	(Z)-PhCH=CHSeMe	67 (56)	6.85	6.5	10.2
	PhSe	120	1 (1)	(Z)-PhCH=CHSePh^{g}	60 (65)	6.9	6.75	10.2
	α-$C_{10}H_7Se$	120	3	(Z)-PhCH=CHSe$C_{10}H_7$-α	63	6.85	6.6	10.2
	p-(Me_2CHS)C_6H_4Se	120	2 (12)^{e}	(Z)-PhCH=CHSeC_6H_4($SCHMe_2$)-p^{h}	75 (72)^{e}	6.95	6.7	10.2
	MeSe	25	1	(E)-PhSCH=CHSeMe	85	6.75	6.25	14.5
	PhSe	25	20	(E)-PhSCH=CHSePh	56	6.75	6.55	14.5
	MeSe	25	1 (5)	(Z)-PhSCH=CHSeMe	74 (85)	6.65^{i}		
	PhSe	25	22	(Z)-PhSCH=CHSePh	65	6.8^{j}		
	MeSe	25	2 (7)	(E)-PhSeCH=CHSeMe	79 (77)	6.9	6.55	15.2
	PhSe	25	24	(E)-PhSeCH=CHSePh	80	6.85		
	MeSe	25	1	(Z)-PhSeCH=CHSeMe	58	6.95^{k}		
	PhSe	25	3	(Z)-PhSeCH=CHSePh	58	7.1^{l}		

[a] The reactions were run in HMPA. The values reported in parentheses refer to the reactions carried out in DMF or DMA. [b] Unless otherwise specified the reaction products were liquids. [c] Based on isolated products after column chromatography and calculated from the amount of vinyl halide employed. [d] These data refer to the chemical shift of the two olefinic protons and to their coupling constant. Unless otherwise specified nmr spectra were recorded in $CDCl_3$ solutions. [e] In DMA. [f] Mp = 61-3°C. [g] Mp = 44-5°C (Litt.[10] Mp = 45-7°C). [h] Mp = 52-4°C. [i] In C_6D_6, δ_A 6.5, δ_B 6.4, J_{AB} = 8.1 Hz. [j] In C_6D_6, δ_A 6.65, δ_B 6.55, J_{AB} = 8.1 Hz. [k] In C_6D_6, δ_A 6.8, δ_B 6.65, J_{AB} = 8.1 Hz. [l] Litt.[11] δ 7.12.

References and Notes

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7) (Z)-PhSCH=CHCl and (Z)-PhSeCH=CHCl were obtained from the reaction of (Z)-CHCl=CHCl with PhSNa and PhSeNa, respectively. The (E)-isomers were instead prepared by adding PhSCl and PhSeCl to acetylene.

8) In every case the reaction mixtures were analyzed by glc and nmr and the reactions were found to be almost completely stereospecific (less than 5% of the undesired stereoisomer was present). The (E)- or (Z)- configurations could be easily assigned on the basis of the value of the coupling constant between the two ethylenic protons.

9) The synthetic interest of these reactions is further increased by the fact that the vinyl methyl selenides can be easily demethylated to give vinyl selenide anions which then react with a variety of halides. Interesting enough these reactions occur with retention of configuration (Unpublished observation from this laboratory).

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